AD-A011 908

VALENCE PHOTOISOMERIZATION OF 1-ETHOXYCARBONYL-1 H-
AZEPINE AND ITS THERMAL REVERSION. QUANTITATIVE ASPECTS

Guilford Jones, II, et al

Boston University

Prepared for:

Office of Naval Research
Advanced Research Projects Agency

15 June 1975

197103

ADA011908

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 2	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Valence Photoisomerization of 1-Ethoxycarbonyl-1H-azepine and Its Thermal Reversion. Quantitative Aspects.		5. TYPE OF REPORT & PERIOD COVERED Technical, 7/1/74 - 5/31/75
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Guilford Jones, II and Laura J. Turbini		8. CONTRACT OR GRANT NUMBER(s) N00014-67-A-0280-0003
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Boston University Boston, Massachusetts 02215		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS ARPA Order No. 2721/1-4-74 Program Code No. 4F10
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217 DODAAD Code N00014		12. REPORT DATE June 15, 1975
		13. NUMBER OF PAGES 29
14. MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office)		15. SECURITY CLASS. (of this report) unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Reproduction in whole or in part is permitted for any purpose of the United States Government. Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Prepared for publication in the Journal of the American Chemical Society

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Photochemical conversion of energy, valence isomerization, solar energy studies, excited states of heterocyclic compounds

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Photolysis of 1-ethoxycarbonyl-1H-azepine in solution at 325 - 385 nm gives a valence isomer with a chemical efficiency of 95% and a quantum efficiency of 0.013. The valence isomer reverts cleanly to azepine at 112 - 145° in an uncatalyzed reaction which is exothermic (ΔH =-10 kcal/mol, 63 cal/g). The valence isomerization can be driven by sunlight and laser emission at 458 nm and cycled in sequential photochemical and thermal steps. The azepine does not luminesce but the energies of S_1 (reactive) and T_1 (unreactive) excited states can be estimated from sensitization and quenching experiments.

OFFICE OF NAVAL RESEARCH

Contract N00014-67-A0280-0003

TECHNICAL REPORT NO. 2

VALENCE PHOTOISOMERIZATION OF 1-ETHOXYCARBONYL-1H-AZEPINE

AND ITS THERMAL REVERSION. QUANTITATIVE ASPECTS

by

G. Jones, II and L. J. Turbini

Department of Chemistry
Boston University
Boston, Massachusetts 02215

June 15, 1975

VALENCE PHOTOISOMERIZATION OF 1-ETHOXYCARBONYL-1H-AZEPINE

AND ITS THERMAL REVERSION. QUANTITATIVE ASPECTS.

Guilford Jones, II* and Laura J. Turbini

Department of Chemistry, Boston University

Boston, Massachusetts   02215

ABSTRACT

Photolysis of 1-ethoxycarbonyl-1H-azepine (3) at 325 - 385 nm gives quantita-
tively the valence isomer, 2-ethoxycarbonyl-2-azabicyclo(3.2.0)hepta-3,6-diene (4).
The quantum yield in benzene is 0.013 and is virtually unchanged in other solvents
including n-propyl bromide and with the addition of triplet quenchers. Sensitization
with fluorenone, benzophenone, or valerophenone does not affect valence isomerization.
Azepine 3 acts as a quencher of the photoelimination of valerophenone (k_q = 7.0 x 10^9
$M^{-1}sec^{-1}$) and the phosphorescence of biacetyl (k_q = 5.3 x 10^8 $M^{-1}sec^{-1}$). Laser
photolysis at 457.9 nm affects isomerization 3 → 4 with a quantum efficiency of 0.013.
On the basis of absorption, sensitization, and quenching data for 3, energies of low
lying excited states are estimated (E_{S_1} = 60 ± 1 kcal/mol and E_{T_1} 55 ± 1 kcal/mol).
Pyrolysis of 4 gives 3 in a clean, exothermic, first order reaction at 113 - 143°
in diglyme-d_{14} (E_a = 28.7 kcal/mol, A = $10^{12.3}$ sec^{-1}) or in hexadecane (k = 4.60 x
10^{-4} sec^{-1}, 127.5°). The mechanism suggested for photochemical isomerization 3 → 4
and its thermal reversion involves a common diradical-zwitterionic intermediate.
Emphasis is placed on the importance of charge separation in such an intermediate,
the geometry of which facilitates radiationless decay from the excited surface to
bicyclic product. Isomerization 3 → 4 may be "cycled" in sequential photochemical
and thermal steps with good chemical efficiency, providing a model for the storage
and conversion of photochemical energy.

The photochemistry of 1,3,5,-cycloheptatriene (1a), its heterocyclic analogs, 1H-azepine (1b) and oxepin (1c), and their derivatives has received considerable attention.[1] A reaction of general importance is valence photoisomerization to bicyclic dienes 2; in many cases the process is thermally reversible. We became interested in the photoisomerization of 1-ethoxycarbonyl-1H-azepine (3), since the reported[1d] behavior of this system showed promise for the storage and conversion of electronic energy. (in principle, a portion of solar energy) In particular, photolysis of 3, which absorbs light in the visible, gives 4 cleanly and photochromicly (with bleaching). Photoisomer 4 is kinetically stable but reverts to 3 in a thermal reaction which is uncatalyzed and apparently exothermic.[1d] We wish to provide quantitative details concerning this isomerization of a sort not generally available for the cyclic trienes, which allow identification of states and suggestions for pathways for photochemical and thermal reaction. The discussion will bear on the relationship between ground and excited state potential surfaces for such systems.

1   2

a, X = CH_2
b, X = NR
c, X = O

3   4
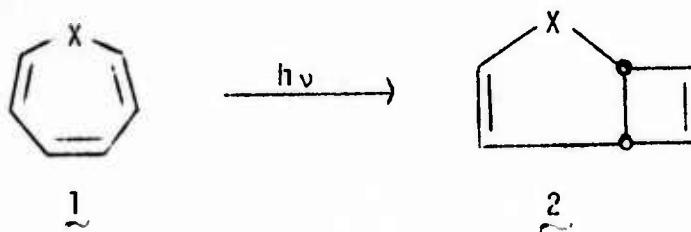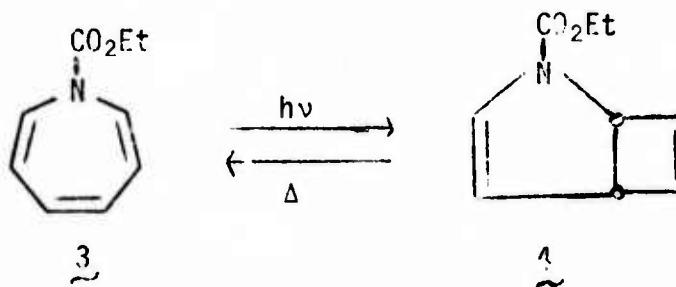
Results

The ultraviolet spectrum of 3^2 displays a weak transition at 330 nm. This absorption, which is blue shifted in polar solvent and probably n, π^* in character,[3] tails into the visible with onset at ~~about 480~~ nm and gives 3 its orange color. Luminescence was not observed for 3, either in benzene at room temperature or in EPA glass at 77°K. Irradiation of 3 at 325-385 nm gave 4 without the appearance of side products (> 97% yield by glc and nmr). Quantum yields for isomerization as a function of solvent and the presence of additives are shown in Table I. Notably, the photolysis was not appreciably altered by (1) moderate concentrations of potential quenchers of excited triplets, 2,5-dimethyl-2,4-hexadiene and cyclooctatetraene, (2) a heavy atom[5] reagent, n-propyl bromide, as solvent, or (3) the addition of dimethylacetylenedicarboxylate (DMAC), a good dipolarophile.[6]

In experiments where photosensitizers, benzophenone (E_T = 69 kcal/mol), fluorenone (E_T = 53 kcal/mol) and valerophenone, absorbed most of the light, photoisomerization of 3 was negligible. That the excited triplet of 3 could in fact be produced was inferred from experiments in which the photoelimination of valerophenone to acetophenone[7] was quenched. Measurement of ϕ_0/ϕ at two concentrations of 3, 4.5 and 6.6 x 10^{-3} M, gave $k_q \tau$ = 56 $\pm$ 8 M^{-1}, from which the quenching constant, k_q = 7.0 x 10^9 M^{-1} sec^{-1}, could be calculated assuming τ (valerophenone) = 8.0 x 10^{-9} M^{-1} sec.[8] For comparison the estimated rate constant for diffusion controlled quenching, according to the modified DeBye equation,[9] in benzene at 30° is 1.8 x 10^{10} $M^{-1} sec^{-1}$, and the "upper limit" quenching constant for dienes in benzene (25°) has been determined in several studies to be 5 x 10^9 $M^{-1} sec^{-1}$.[9] Quenching of the phosphorescence of biacetyl with 1.0 - 4.0 x 10^{-5} M azepine was observed at room temperature. From the plot of ϕ_0/ϕ vs. [3], $k_q \tau$ = 2.5 $\pm$ 0.3 x 10^5 M^{-1} was obtained, from which k_q = 5.3 x 10^8 $M^{-1} sec^{-1}$ could be calculated assuming τ (biacetyl) = 4.6 x 10^{-4} sec.[10]

Table 1. Quantum Yields for Photoisomerization $3 \rightarrow 4$.

[3]	Solvent	Additives (M)	ϕ^a
0.08	cyclohexane	----	0.010
0.09	diglyme[b]	----	0.013
0.10	Benzene	----	0.013
0.03	n-propyl bromide	----	0.013
0.08	benzene	COT[c] (0.11)	0.014
0.10	benzene	diene[d] (0.02 - 0.08)	0.012
0.10	benzene	fluorenone[e] (0.9)	<0.003[g]
0.09	benzene	benzophenone[f] (1.0)	<0.003[g]
0.007	benzene	valerophenone[f] (0.4)	<0.003[g]
0.03	benzene	DMAC[h] (0.08)	0.010[i]

[a]Rayonet reaction (355 ± 30 nm), 30 ± 1°C, valerophenone actinometer (ref 4), estimated error, ± 15%. [b]bis(2-methoxyethyl) ether. [c]Cyclooctatetraene. [d]2,4-dimethyl-2,5-hexadiene. [e]Sensitizer absorbed 88% of light. [f]Sensitizer absorbed 75% of light. [g]Upper limit corrected for azepine absorption. [h]Dimethyl acetylenedicarboxylate. [i]Some light absorption by DMAC.

Sealed ampoule pyrolysis of 4 proceeded nearly quantitatively in solvents at temperatures above 100°. Appearance of 3 (nmr analysis) was smoothly first order over two half-lives. The results are shown in Table 2 along with activation parameters for pyrolysis in diglyme-d_{14}. The kinetics are in good agreement with the approximate rate data for pyrolysis of neat 4, reported by Paquette and Barrett[1d] from which k $(4 \rightarrow 3, 126.5°) = 6.6 \times 10^{-4}$ sec^{-1} may be calculated.

Table 2. Kinetics of the Thermally Induced Isomerization $4 \rightarrow 3$

Solvent	Temperature (°C)	$k \ (10^4 \ sec^{-1})$	
diglyme-d_{14}	112.5	1.45 ± 0.06	
	122.5	3.44 ± 0.15	
	127.5	5.34 ± 0.05	$E_a = 28.7$ kcal/mol
	133.0	8.21 ± 0.58	$A = 10^{12.3} \ sec^{-1}$
	142.5	19.3 ± 0.11	
hexadecane	127.5	4.60 ± 0.44	

The photoisomerization $3 \rightarrow 4$ could be affected in direct sunlight and with use of an argon ion laser. The quantum yield for isomerization at 457.9 nm in benzene was 0.013. The valence isomers could be "cycled". A sealed Pyrex tube containing 3 and 4 in diglyme-d_{14} was alternately irradiated (sunlight or near UV) and pyrolized (generally 130°). The isomerizations were followed to high conversion by nmr (benzene internal standard). Although the photochemical step was extraordinarily clean, the back reaction built up a small amount of byproduct (dimer[11] or polymer), such that after ten passes material balance was about 50%.

Discussion

The failure of dienes, 2,4-dimethyl-2,5-hexadiene (E_T < 53 kcal/mol[12]), a well known efficient quencher of reasonably long lived excited triplets,[9] and COT, for which a very low triplet energy has been calculated,[13] to alter the photolysis of 3 implicates a reactive singlet state for valence isomerization. The sensitization data, in which common energy transfer agents representing a range of triplet excitation energies (E_T 53 - 73 kcal/mol[14]) are ineffective, confirm that a singlet state (probably of n,π^* character) is responsible for formation of 4. The quenching of valerophenone photoelimination at a rate near the diffusion limit further establishes that a triplet state of 3 is accessible but unreactive. That datum and the inefficiency with which 3 quenches the phosphorescence of biacetyl (E_T = 55 - 56 kcal/mol[16]) bracket the energy of the lowest triplet of azepine at ∿ 55 kcal/mol.[17]

The n,π^* absorption for 3 (λ_{max} 330 nm, tailing past 450 nm) and the success of laser photolysis at 453 nm (61 kcal/Einstein), a wavelength which must be very close to the 0-0 transition, narrow the acceptable range for the energy of S_1. Values of E_{S_1} = 60 ± 1 and E_{T_1} = 55 ± 1 kcal/mol would be consistent with the data and allow for a reasonable n,π^* singlet-triplet separation. This placement of singlet and triplet levels may be of general use for the heterocyclic triene systems in the absence of luminescence data.

Interestingly, the existence of a very low lying triplet (e.g., E_T < 50 kcal/mol), analogous to "aromatic" species (π,π^* triplets) predicted for cyclic polyenes having formally 4n cyclic electronic arrays which enjoy resonance stabilization,[13] or analogous to triplet 1a (E_T = 47 kcal/mol[1c]) appears unlikely for 3. On the other hand, it is improbable that the π,π^* triplet would lie much above 60 kcal/mol if 3 be diene-like.[11] Further speculation is (1) that the n,π^* and π,π^* triplet levels are closely spaced (slightly below the S_1 n,π^* level) (2) that intersystem crossing to the higher lying π,π^* state is facile[18] and accounts at least in part for the low efficiency of valence isomerization and (3)

that the effect of heavy atom solvent on the quantum yield is minimal since
depletion of S_1 through intersystem crossing is intrinsicly rapid.[19]

Data for 3 completes an excited state structure - reactivity pattern (Table
3) for several cyclic polyene systems which have been the object of comparison in
numerous studies.[20] Excited singlets in the series are uniformly reactive (al-
beit inefficiently where measured), whereas triplets do not bring about valence
isomerization.[24] The latter is noteworthy in view of the established reactivity
under sensitization conditions of diverse seven and eight membered conjugated cyclic
dienes and trienes such as 1,3-cyclooctadiene,[25] cyclohepta-3,5-dien-1-one,[26] a deri-
vative of 2-aza-1,3-cycloheptadiene,[27] and including cycloocta-2,4,6-trien-1-one[23]
(where the reactive state is most likely a triplet for direct irradiation). A mech-
anism considered for valence isomerization in each case involves cis-trans isomeri-
zation via the excited triplet to a strained ring system (with formally one trans
double bond), which ring-closes to bicyclic product in a symmetry unrestricted
thermal reaction. Such a course for trienes 1 is shown below in which 5 is one
of several possible geometric photoisomers of 1. In two of the previous studies,[25,23]
the intermediate analogous to 5 has been either isolated or trapped. The failure
of triplets of 1 to give bicyclic product probably reflects the relatively more

1
a, X = CH₂
b, X = O
c, X = NR

5

2
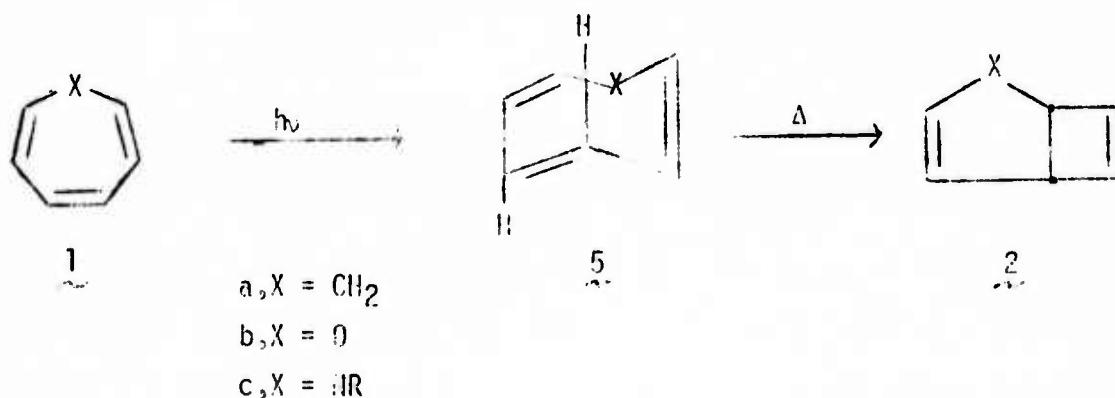
Table 3. Photolysis and Pyrolysis Characteristics for Selected Reversible Valence Isomerizations.[a]

Cyclic Polyene $\xrightarrow{h\nu}_{\Delta}$ Bicyclic Diene		Direct Irradiation	Sensitized Irradiation	Ref	E_a, kcal/mol[d]	(ref)
1a	2a	X ($\emptyset = 0.010$)	0	1a,c	39.5	(21)
1c	2c	X	0	1h	---	
3	4	X ($\emptyset = 0.013$)	0	This work	23.7	This work
COT[b]	BOT[c]	X	0	22	13.7	(23)

[a] X = isomerization of polyene observed; 0 = isomerization of polyene unobserved.
[b] 1,3,5,7-cyclooctatetraene. [c] Bicyclo(4.2.0)octa-2,4,7-triene. [d] Activation parameters for thermal back reaction.; log A values for 2a, 4, and BOT are 14, 12.3, and 12.0, respectively.

severe restrictions due to bond angle strain in 5 compared to the other twisted cyclopolyenes (molecular models show this impressively). Triplet COT may indeed reach a configuration analogous to 5 but the overall result is formation of semi-bullvalene. [22c]

Excited singlets of 1 may give intermediates 5 prior to valence isomerization. Indeed there is direct evidence that 1,3,5-cyclooctatriene $(6)^{29}$, 1,2,4,7-tetra-phenylcyclooctatetraene $(7)^{30}$ and 1,3-cyclooctadiene $(8)^{31}$ give geometric isomers on direct irradiation. The isomers of 6 and 8 may lead to valence isomeric bicyclic polyenes, while the isomer of 7 may be responsible for formation of diphenylacetyl-ene and p-terphenyl (via a bicyclic triene). [30b] However, Hebe and Fonken have shown that 8 gives 9 under conditions where geometric isomer 10 is stable. In addi-tion, thermal reversion to 7, from its geometric photoisomer is "quantitative", [30a] meaning that valence photoisomerization of 7 by way of a geometric isomer is extreme-ly inefficient if not absent.

The point here is that in the singlet manifold for the cyclic dienes and trienes, there exists a path for ring closure to a bicyclic isomer which does not re-quire formation of a geometric isomer. For the cyclic polyene triplets valence isomerization proceeds through prior cis-trans isomerization and thermal ring closure, but where the geometric isomer is accessible on geometric grounds (not the
only
case for trienes 1) and reactive enough to give bicyclic product under photolysis conditions (marginally the case for 8^{31}). [32] After examination of the thermal sur-face for 4 → 3, we will return to the mechanism of singlet valence isomerization of 3.
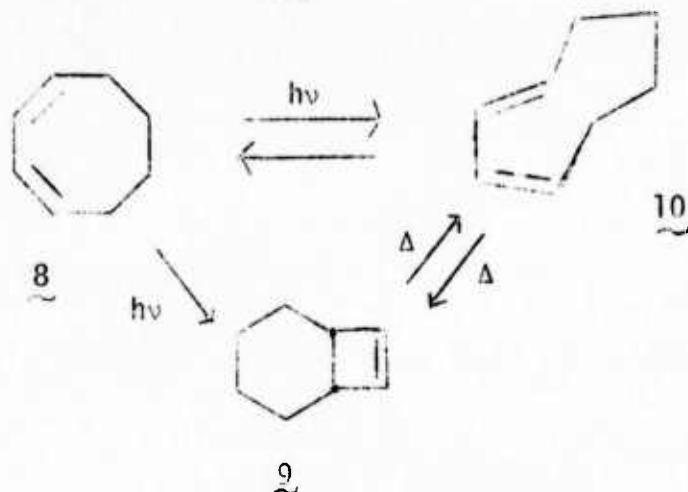
Circumstantial arguments may be brought against two mechanisms for the thermal isomerization $4 \rightarrow 3$. The first mechanism involves formation of 5 _via_ conrotatory ring opening of 4, following the suggestion of Baldwin and Kaplan[33] in their study of ring openings of bicyclic dienes. Such a mechanism is apparent in the thermal degenerate rearrangement which accompanies valence isomerization of deuterium label-ed bicyclo(4.2.0)octa-2,7-diene[34] and in the pyrolytic ring opening of 9.[35] The evidence for the appearance of cis-trans isomers comes again for the more flexible ring systems, in fact those cases where the strained geometric isomers are avail-able photochemically from the all-cis cyclic polyenes.[25,29,31] The acceleration of pyrolysis for 4 compared to 1a does not support a general mechanism involving a cis,trans,cis intermediate. Aside from the geometric difficulties in 5, it is difficult to see how the energy barrier for ring opening of 4 (an overall rate determining, symmetry unrestricted step which would respond more likely to steric and bond angle strain effects than to electronic effects) could be reduced by 11 kcal/mol by substituting -NR- for $-CH_2-$.

Thermal disrotatory ring opening of 4 may give 3 directly in a concerted pro-cess. It is apparent from the magnitude of the activation energy for valence iso-merization (Table 3) that BOT enjoys significant six-electron transition state stabil-ization (11) (for disrotatory opening, a 6e Huckel[36] aromatic[37] system) and suffers

little from four-electron destabilization such as in 12 (a 4e Huckel, antiaromatic transition state).[33] Ring opening of 4 could likewise benefit from the importance of 13, to the extent that the lone pair on nitrogen could contribute to a pyrrole-like aromatic sextet.[39]
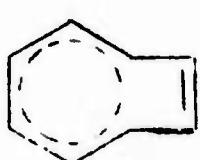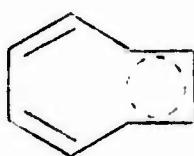
$\underset{\sim}{11}$ $\underset{\sim}{12}$ $\underset{\sim}{13}$

However, the heteroatom substituent effect appears to be more general and manifest in accelerations of thermal disrotatory ring openings of fused cyclobutenes in which a stabilizing six electron transition state cyclic array is not available. For example 14 is thermally stable, while 15 ring opens readily.[40] Likewise cyclo-adducts 16 of dimethyl acetylenedicarboxylate and cyclic enamines are generally un-stable even near room temperature with respect to ring opening to 17.[41]
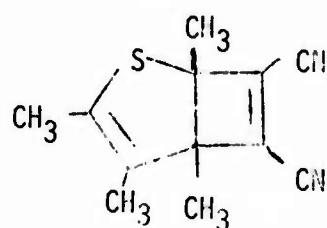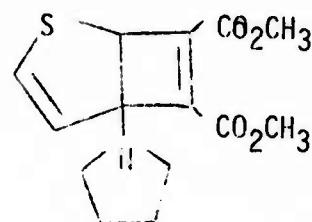
$\underset{\sim}{14}$ $\underset{\sim}{15}$
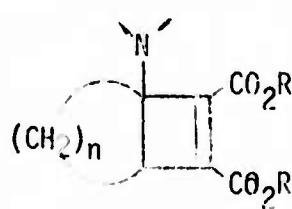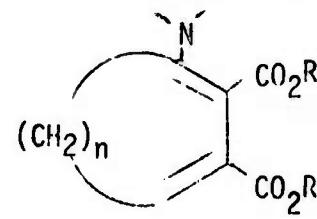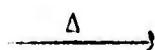
$\underset{\sim}{16}$ $\underset{\sim}{17}$

We prefer a mechanism for the thermal isomerization $4 \rightarrow 3$ involving a non-synchronous ring opening in which all-cis 3 emerges following motions which are overall dirotatory but where pi bond development in 3 lags bond breaking in 4 early along the reaction coordinate. In the extreme a two step path including di-
(geometry unspecified)
radical intermediate 18 would be important. Orbital overlap for such a species (from 4, 15, or 16)as in 19 might be important. O'Neal and Benson[42] have suggested a diradical path for ring opening of bicyclo(3.2.0)hept-6-ene (a fused cyclobutene similar to 4), and the activation parameters for the isomerization $2a \rightarrow 1a$ have been considered not inconsistent with the diradical formulation.[21] Our analysis respects the basic similarity between isomerizations $2 \rightarrow 1$ and the disrotatory cyclobutene $\rightarrow$ 1,3-butadiene ring opening, an interconversion of "lumomers,"[43] for which an orbital crossing and a diradical intermediate are predicted with support from semi-empirical calculation of the isomerization potential surface.[44]
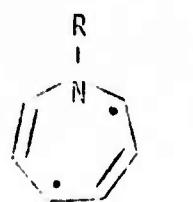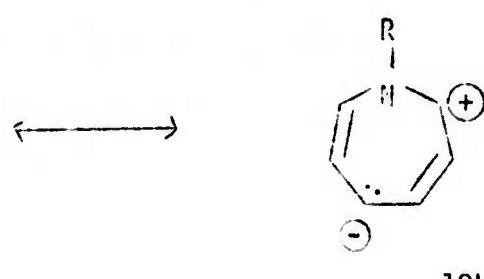
18a $\longleftrightarrow$ 18b

$\xrightarrow{\Delta}$

19
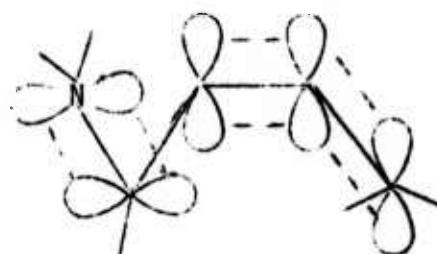
Diradical 18 may well have more complicated electronics than that associated with canonical form 18a (product of homolytic ring opening). The transition state for formation of the latter would be stabilized relative to that for 2a by an amount associated with the degree to which the carboxamido group (RCONR'-) stabilizes a radical center. This value is unknown but may be approximated by the effect of the acyloxy (RCO$_2$-) substituent on C-H bond dissociation energies (ΔBDE < 1 kcal/mol).[45] The reduction in activation energy for 4 vs. 2a (11 kcal/mol) is inconsistent with this kind of transition state stabilization. An alternative view recognizes the extent to which the odd electron centers in 18 interact with adjacent polarizing fragments (e.g., 19). Respecting the electron releasing ability of nitrogen, contributing structures of the type 18b gain importance and in molecular orbital terms the singlet diradical wave function has considerable ionic character.[46] In the extreme, intermediate 18 would be a discrete zwitterion as suggested by Criegee and coworkers[47] for ring opening of highly polarized cyclobutenes. Epiotis has also pointed out the importance of polarizing substituents on the rates of electrocyclic reactions.[48,49]

Quantitative estimation of transition state stabilization due to charge separation (i.e., the importance of 18b) for pyrolytic cyclobutene ring openings is difficult. It would depend of course on substituent polarizing ability and interaction with solvent. A solvent effect on the rate of pyrolysis of 4 (Table 2) is absent; however, in several studies in which 1,3 or 1,4 dipoles have been implicated, modest solvent dependence has been observed.[50] On the other hand, the substituent effect on the rate of ring opening of 15 and 16 appears to be quite large,[51] whereas substituent influence in 4 is predictably[39] intermediate.

The formulation of an intermediate (a secondary minimum) for the ground state surface 4 → 3 is important in terms of current theories concerning modes of reactive

radiationless decay of excited species. We propose an energy surface relationship
as shown in the Figure , which is consistent with photochemical and thermal data
and includes all experimental quantities which are readily accessible. (The heat
of reaction $4 \to 3$ has been measured by differential scanning calorimetry.[52])

The scheme submits to the following considerations. (1) Isomerization $3 \to 4$
is a G-type photochemical reaction[53] in which adiabatic formation of the excited
state of product is energetically prohibited[54] and dissociation into fragments is
not important. (2) The aforementioned similarity with cyclobutene ring opening
requires that the ground state isomerization $4 \to 3$ be "forbidden" involving at some
point along the reaction coordinate a formal HOMO-LUMO orbital crossing.[43] (3) The
orbital crossing or avoided crossing[55] provides an orbitally degenerate (diradical)
ground state in proximity with a minimum or "funnel"[56] in the excited singlet mani-
fold,radiationless transition between which is facilitated. (4) The minimum in the
triplet surface will occur at a loose geometry (flexible somewhat flattened ring)
resembling more the boat-like ground state of 3, whereas the minimum or funnel in
the singlet surface will assume a tight geometry (more folded or "pinched", less
flexible ring, the geometry of diradical 18) resembling more the ground state of 4.[56]

Decay from S_1 proceeds with little or no activation (no accompanying fluore-
scence) by way of mixing with an upper doubly excited singlet, the actual state
of intended crossing with the ground configuration.[57] The inefficiency of valence
isomerization may be understood in terms of competing intersystem crossing to T_1
(vide supra, provided that S_1 reach some minimum which would allow time for spin
flipping) or in terms of uneven partitioning of an intermediate (18) (favoring 3
over 4), as expected in view of the skewed nature of the energy storing ground sur-
face.[58]

Consideration of ionic character for 18 provides an explanation for the
accelerated rate of pyrolysis of 4 and other polarized cyclobutenes confined to dis-
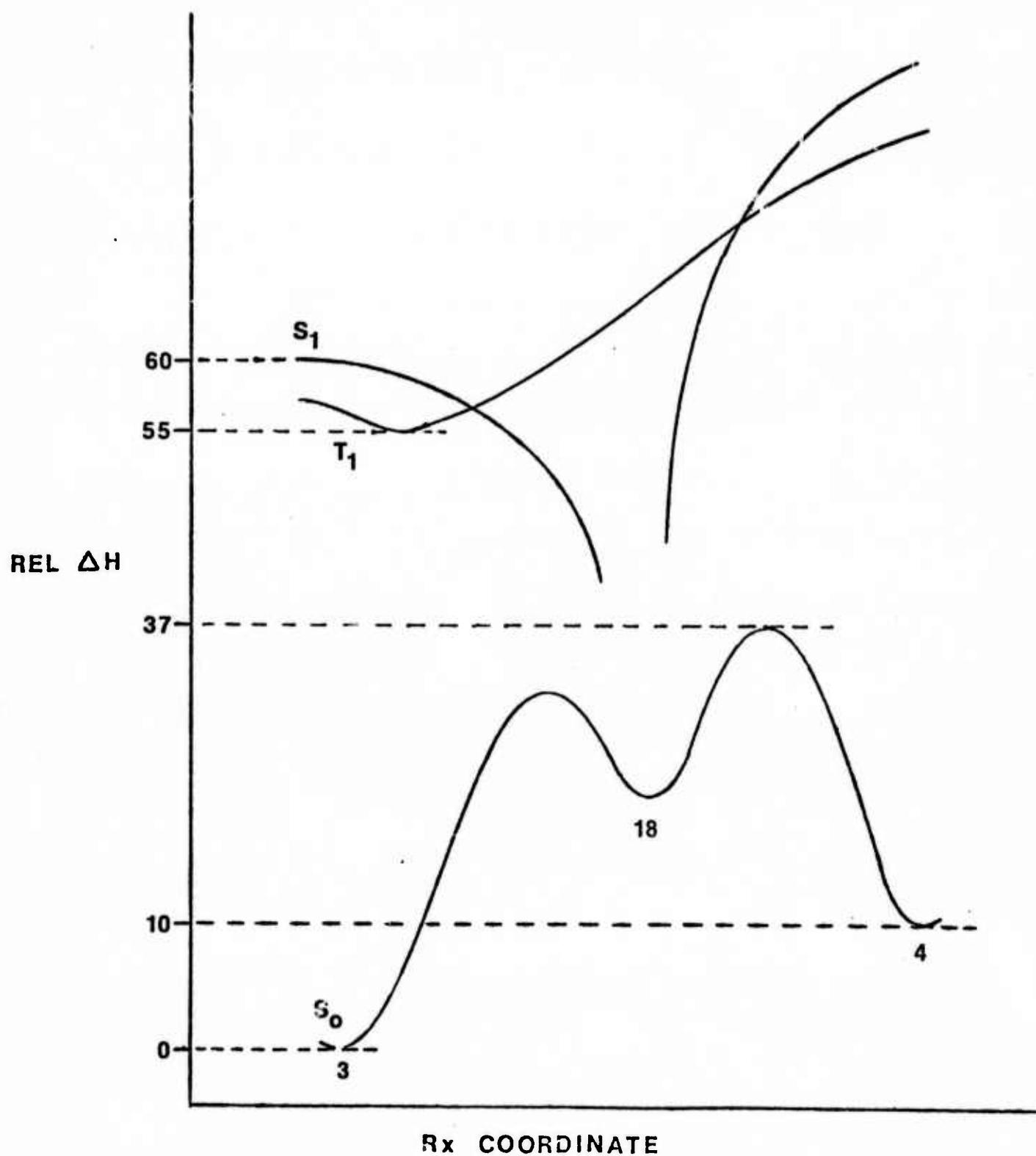
Figure. Potential energy surfaces for the photochemical and thermal interconversions of 3 and 4.
$\Delta H^{\ddagger}(4 \rightarrow 3, 128°) = 27$ kcal/mol.

rotatory ring opening. Development of charge appears to be important for photo-chemical ring closure as well. Electron releasing substituents are known to en-hance valence isomerization of cycloheptatrienes[59] and tropones.[60] This structure-reactivity pattern implicates generally a ground-excited energy surface relation-ship in which the excited surface is increasingly directed (funnelled) to a tighter geometry at which radiationless transition occurs (making valence isomerization more favorable) as the diradical ground state becomes more ionic.[56,61] The excited triplet is correspondingly ineffective in bringing about valence isomerization be-cause its minimum will occur at a loose geometry inappropriate for ring closure to bicyclic product.

The depth of the potential well for 18 will depend on solvent and substituent stabilization of charge and is of unknown size.[62] Efforts to trap such a species generated photochemically with a good dipolar ile, DMAC, were not successful. This places a short but uncertain lifetime on 18; if the quantum efficiency for 3 depends solely on partitioning of 18, a barrier of about 3 kcal/mol would be re-quired leading to 4.[58]

In summary, the reactive state for photochemical valence isomerization $3 \rightarrow 4$ has been identified as an n,π^* singlet with a $S_0 - S_1$ energy separation of about 60 kcal/mol. The lowest triplet of 3 is unreactive and has an energy above ground state of about 55 kcal/mol. Mechanisms for photolysis $3 \rightarrow 4$ and pyrolysis $4 \rightarrow 3$ are complimentary, in that the "forbidden" nature of the thermal reaction provides a region of surface into which the excited singlet funnels or near which there is an excited state minimum for facile radiationless decay. This region of surface near the formal crossing for ground and excited configurations is best formulated as a diradical-zwitterion (18). Partial charge developed and stabilized in such a species is important not only in lowering the barrier for pyrolysis $(4 \rightarrow 3)$ but

also in providing a tight geometry, facilitating photochemical ring closure to~~bi-~~ energy-rich

cyclic product (3 → 4). The results and suggested mechanism have implications for

the isomerization of cyclic trienes (1 → 2) generally and provide another look at

a thermally reversible~photochemical process. Systems of this sort, for which endoergic

extensive experimental detail is available, are still rare. They supply uniquely

information for the evaluation of surface relationships which is of current

theoretical interest, and in a practical vein they provide prototypes   for

the photochemical storage and conversion of radiated (solar) energy.

Experimental Section

General. 1-Ethoxycarbonyl-1H-azepine (3)[2] was photolyzed in acetonitrite on a

preparative scale (Hanovia immersion apparatus) to give 4 following generally the

procedure of Paquette and Barrett.[1d]

Benzene, cyclohexane and n-propyl bromide were purified for use in photolysis

by washing with 1) sulfuric acid 2) aqueous $NaHCO_3$ and 3) distilled water followed

by distillation from P_2O_5 or sodium. Valerophenone (Aldrich) was distilled under

reduced pressure. Biacetyl was purified by spinning band distillation (bp 87-88°).

Diglyme was distilled over sodium. Cyclooctatetraene, 2,4-dimethyl-2,5-hexadiene,

fluorenone, and dimethyl acetylenedicarboxylate were commercial reagent grade mater-

ials used as received.

Varian 920 (tc detector) and 1400 (fi detector) instruments were used for ana-

lytical glc. Columns employed were (A) 5 ft x 1/4 in, 3% SE 30 on 100/120 Varaport-

30 and (B) 8 ft x 1/8 in, 3% FFAP on Chrom-W.

Quantum Yields. Solution samples in 15 mm stoppered cylindrical Pyrex tubes were

irradiated in a Rayonet chamber reactor (Model RPR 204) equipped with RUL 3500A lamps and a merry-go-round accessory (Model MGR 100) (Southern New England Ultraviolet Co.). Samples were purged with nitrogen prior to irradiation. Solutions of 3 in the appropriate solvents (with additives) were irradiated in parallel with valerophenone (0.4 M in benzene) which served as actinometer and for which a quantum yield of production of acetophenone of 0.33^{A} was assumed. Concentrations for all parallel irradiation samples were employed which insured complete absorption (measured absorbance > 1 at 0.1 path maximum) over the range of lamp emission (325-385 nm). Samples were analyzed by glc for the appearance of 4 (column A, 100°, vs. 3) and acetophenone (column B, 150°, vs. dodecane internal standard). Quantum yields are averages of at least two runs at low conversions of valerophenone ($\sim$15%) and 3 (5-10%). Statistical analysis of area ratios for 4 (area from cut out and weigh procedure) and acetophenone (area from disc integration) in replicate runs indicated a precision of $\pm$ 15%.

Quenching of Valerophenone Photoelimination. The appearance of acetophenone from valerophenone was monitored as previously indicated for samples of valerophenone in benzene with increasing concentrations of 3. Relative amounts of acetophenone formed, obtained with good precision ($\pm$ 5%), were used for $\emptyset_0/\emptyset$. Values were corrected for competitive absorption by 3 by computing relative absorbances at several wavelengths in the region of lamp emission. This correction became significant at higher concentrations of 3, and at lower concentrations, values of $\emptyset_0/\emptyset$ were within experimental error of 1.0; therefore, quenching behavior was assessed only over a limited range.

Luminescence Experiments and Biacetyl Phosphorescence Quenching. Using an Hitachi Model MPF fluorescence spectrophotometer, emission from 3 was undetectable for samples at room temperature (0.02 M in benzene) and at 77°K (EPA glass, 0.001M).

The phosphorescence emission of biacetyl in benzene (λ_{max} 522 nm) at room tempera-
ture was monitored as a function of 3. Samples were degassed through several
freeze-thaw cycles on a vacuum line. Relative intensities at the emission maximum
gave $\emptyset_o/\emptyset$. The fluorescence of biacetyl was not quenched with the addition of 3.

Pyrolysis Experiments. Samples of 4 in diglyme-d_{14} or hexadecane (with benzene
internal standard) were degassed in cleaned medium wall Pyrex nmr tubes (Wilmad Co.).
Sealed ampoules were pyrolyzed in an insulated oil bath, thermostated using a Therm-
o-watch (Instruments for Research and Industry) and a calibrated ASTM thermometer.
Temperature fluctuation was < 0.5°. Ampoules were quenched and analyzed by nmr.
Formation of 3 was followed by the appearance of a multiplet at 5.58 (vinyl C - H)
and disappearance of 4 was monitored with reference to signals at 4.9 and 5.2 δ
(multiplets, C_1 and C_4^{1d}). In experiments where benzene signal integration was used
as an internal standard, a material balance for isomerization of > 95% was obtained.
Rate constants were calculated from the integrated first order rate equation and
errors are average deviations for at least four points at each temperature.

Laser Photolysis of 3. Samples of 3, 0.1 M in benzene, were irradiated with an
argon ion laser (Spectra-Physics, Model 164). The emission at 457.9 nm (rated at
250 mW) was focused on the optically flat circular window of a standard 5 cm Pyrex
cell containing sample. Beam intensity was checked by irradiation of a 10 cm cell
containing potassium ferrioxalate[64] actinometer solution. The quantum yield for
appearance of Fe(II) was assumed to be 0.95. Concentrations of sample and actino-
meter solutions were employed which insured complete absorption of incident light.
With a beam intensity of 1.05 $\pm$ 0.05 mE/hr, a measureable conversion of 3 → 4 was
observed (glc analysis) in 4 hr. The calculated quantum yield for isomerization
was 0.013 $\pm$ 0.004.

References and Notes

(1) For leading references see (a) L.B. Jones and V.K. Jones, Fortschritte der Chem. Forschung, 13, 307 (1969); (b) O.L. Chapman, Adv. in Photochem., 1, 323 (1963); (c) R. Srinivasan, ibid., 4, 113 (1966); (d) L.A. Paquette and J.H. Barrett, J. Amer. Chem. Soc., 83, 1718 (1966); (e) L.A. Paquette in "Nonbenzenoid Aromatics," vol. 1, J.P. Snyder, Ed., Academic Press, N.Y., 1969, p. 249. (f) J.S. Swenton, K.A. Burdett, D.H. Madigan, and P.D. Rosso, J. Org. Chem., 40, 1280 (1975); (g) G. Kan, M.T. Thomas, and V. Snieckus, Chem. Comm., 1022 (1971); (h) J.M. Holouka and P.D. Gardner, J. Amer. Chem. Soc., 89, 6390 (1967).

(2) R.J. Cotter and W.F. Beach, J. Org. Chem., 29, 751 (1964).

(3) L.A. Paquette, D.E. Kuhla, J.H. Barrett, and R.J. Haluska, J. Org. Chem., 34, 2866 (1969).

(4) P.J. Wagner, P.A. Kelso, and R.G. Zepp, J. Amer. Chem. Soc., 94, 7480 (1972).

(5) For recent reference on heavy atom solvent effects on the course of photochemical reactions, see (a) D.O. Cowan and J.C. Koziar, J. Amer. Chem. Soc., 97, 249 (1975); (b) R.H. Fleming, F.H. Quinn, and G.S. Hammond, ibid., 96, 7738 (1974); (c) W.I. Ferree, Jr., B.F. Plummer, and W.W. Schloman, Jr., ibid., 16, 7741 (1974); and (d) S.P. Pappas and R.D. Zehr, Jr., ibid., 93, 7112 (1971).

(6) R. Huisgen, W. Scheer, and H. Huber, J. Amer. Chem. Soc., 89, 1753 (1967).

(7) P.J. Wagner, J. Amer. Chem. Soc., 89, 5898 (1967).

(8) P.J. Wagner and A.E. Kemppainen, J. Amer. Chem. Soc., 89, 5898 (1967).

(9) For a discussion, see P.J. Wagner and I. Kochevar, J. Amer. Chem. Soc., 90, 2232 (1968) and ref cited therein.

(10) N.J. Turro and R. Engel, J. Amer. Chem. Soc., 91, 7113 (1969).

(11) L.A. Paquette, J.H. Barrett, D.E. Kuhla, J. Amer. Chem. Soc., 91, 3616 (1969).

(12) R.E. Kellogg and W.T. Simpson, J. Amer. Chem. Soc., 87, 4230 (1965).

(13) N.C. Baird, J. Amer. Chem. Soc., 94, 4941 (1972); the actual $S_0 - T_1$ gap will be larger than that calculated for planar COT (27 kcal/mol) when the equilibrium conformation of the ground state is considered.

(14) The triplet energy for valerophenone lies probably within the range found for a number of phenones ($E_T = 73 \pm 2$ kcal/mol).[15]

(15) (a) P.J. Wagner, M. May, and A. Haris, Chem. Phys. Lett., 13, 545 (1972); (b) J.N. Pitts, Jr., D.R. Burley, J.C. Mani, A.D. Broadbent, J. Amer. Chem. Soc., 90, 5902 (1968); (c) D.R. Kearns and W.A. Case, ibid., 88, 5087 (1966).

(16) (a) W.G. Herkstroeter, A.A. Lamola, and G.S. Hammond, J. Amer. Chem. Soc., 86, 4537 (1964); (b) H.L.J. Backstrom and K. Sandros, Acta Chem. Scand., 12, 823 (1958).

(17) For a discussion of the necessary exothermicity for diffusion controlled energy transfer, see ref 12.

(18) (a) M.A. El-Sayed, Accounts Chem. Res., 4, 23 (1971); (b) S.K. Lower and M.A. El-Sayed, Chem. Rev., 66, 199 (1966).

(19) To check for intersystem crossing, a triplet counting experiment was performed. Azepine 3   sensitized   the dimerization of 1,3-cyclohexadiene (E_T = 51 - 52 kcal/mol[11]) with no more than 1/10 the efficiency of benzophenone (in fact very little if any sensitization by azepine was observed). For de-

tails concerning parallel irradiation and nmr analysis for triplet counting, see S.G. Cohen, G.A. Davis, and W.D.K. Clark, J. Amer. Chem. Soc., 94, 869 (1972). Either intersystem crossing for 3 is not important, or energy transfer from triplet 3 is insufficiently exothermic, or triplet 3 is too short lived to be quenched by diene.

(20) See for example ref 1e.

(21) H.R. Willcott and E. Goerland, Tetrahedron Lett., 6341 (1966).

(22) (a) G.J. Fonken, Chem. Ind. (London), 1625 (1963); (b) E. Migirdicyan and S. Leach, Bull Soc. Chim. Belges, 71, 845 (1962); (c) Zimmerman and Iwamura did not find BOT on irradiation under somewhat different conditions and showed that COT gives semibullvalene upon sensitization; H.E. Zimmerman and H. Iwamura, J. Amer. Chem. Soc., 92, 2015 (1970).

(23) E. Vogel, H. Kiefer, and W.R. Roth, Angew. Chem. Int. Ed., 3, 442 (1964).

(24) Photochemical pathways other than four-electron valence isomerization are well known, notably sigmatropic rearrangement for cycloheptatrienes,[1a] formation of phenol from oxepin,[1h] and semibullvalene from COT.[17c]

(25) R.S.H. Liu, J. Amer. Chem. Soc., 89, 112 (1967).

(26) D.I. Schuster and D.J. Blythin, J. Org. Chem., 35, 3190 (1970).

(27) T.H. Koch and D.A. Brown, J. Org. Chem., 36, 1934 (1971).

(28) L.L. Barber, O.L. Chapman, and J.D. Lassila, J. Amer. Chem. Soc., 91, 531 (1969).

(29) T.D. Goldfarb and L. Lindquist, J. Amer. Chem. Soc., 89, 4588 (1967).

(30) (a) E.H. White, E.W. Friend, R.L. Stern, H. Maskill, J. Amer. Chem. Soc., 91, 523 (1969); (b) E.H. White and R.L. Stern, Tetrahedron Lett., 193 (1964).

(31) W.J. Hebe and G.J. Fonken, J. Amer. Chem. Soc., 91, 1249 (1969).

(32) (a) For a thorough discussion of photodecomposition pathway dependence on multiplicity for mono- and bicyclic unsaturated ketones, see D.I. Schuster

and C.W. Kim, J. Amer. Chem. Soc., 96, 7437 (1974); (b) For other triplet isomerizations in rigid bicyclic systems clearly not involving geometric isomers, see R.C. Hahn and R.P. Johnson, J. Amer. Chem. Soc., 97, 212 (1975) and C.W. Jefford and F. Delay, ibid., 97, 2272 (1975).

(33) J.E. Baldwin and M.S. Kaplan, J. Amer. Chem. Soc., 94, 668 (1972).

(34) J.E. Baldwin and M.S. Kaplan, J. Amer. Chem. Soc., 93, 3969 (1971).

(35) J.J. Bloomfield and J.S. McConaghy, Tetrahedron Lett., 3723 (1969).

(36) H.E. Zimmerman, Accounts Chem. Res., 4, 272 (1971).

(37) M.J.S. Dewar, Angew. Chem. Int. Ed. Eng., 10, 761 (1971).

(38) BOT undergoes substantially accelerated ring opening compared to bicyclo-(4.2.0)octa-2,4-diene ($\Delta H^{\ddagger}$ = 25 kcal/mol) in which potential 4e destabilization is absent; see, R. Huisgen, G. Boche, A. Dahmen, W. Hechtl, Tetrahedron Lett., 5215 (1968).

(39) (a) Cyclic delocalization of the nitrogen lone pair in [13] annulenes as a function of the substituent on nitrogen has been assessed; the $-NCO_2Me$ shows diminished electron availability; see A.G. Anastassiou, R.L. Elliott and E. Reichmanis, J. Amer. Chem. Soc., 96, 7823 (1974); (b) For comparison, cyclic delocalization in pyrrole appears to be about two-thirds as important as in benzene in terms of calculated resonance energies; see B.A. Hess and L.J. Schaad, Tetrahedron, 28, 3657 (1972).

(40) D.N. Reinhoudt, H.C. Volger, C.G. Kouwenhoven, H. Wynberg, and R. Helder, Tetrahedron Lett., 5269 (1972).

(41) K.C. Brannock, R.D. Bupitt, V.W. Goodlett, and J.G. Thweatt, J. Org. Chem., 28, 1464 (1963).

(42) H.E. O'Neal and S.W. Benson, Int. J. Chem. Kinetics, 2, 423 (1970).

(43) (a) M.J.S. Dewar, S. Kirschner, H.W. Kollmar, J. Amer. Chem. Soc., 96, 5240

(1974); (b) M.J.S. Dewar and S. Kirschner, ibid., 96, 5244 (1974).

(44) M.J.S. Dewar and S. Kirschner, J. Amer. Chem. Soc., 96, 6809 (1974).

(45) R.K. Solly and S.W. Benson, Int. J. Chem. Kinetics, 3, 509 (1971).

(46) (a) L. Salem and C. Rowland, Angew. Chem. Intern. Ed. Engl., 11, 92 (1972);
     (b) L. Salem, Pure Appl. Chem., 33, 317 (1973); (c) J. Michl, Mol. Photochem.,
     4, 257 (1972); (d) E.F. Hayes and A.K.Q. Siu, J. Amer. Chem. Soc., 93, 2090
     (1971); (e) C.R. Flynn and J. Michl, ibid., 96, 3280 (1974).

(47) R. Criegee, D. Seebach, R.E. Winter, B. Borretzen, H.-A. Brune, Chem. Ber.,
     98, 2339 (1965).

(48) N.D. Epiotis, Angew. Chem. Intern. Ed. Engl., 13, 751 (1974).

(49) Epiotis[48] notes that the predicted acceleration in rate due to polarizing
     substitution should be greater for conrotatory vs. disrotatory cyclobutene
     ring opening. Even with this salutary electronic effect on the formation of
     5, its importance for pyrolysis of 2 remains unappealing due to its certain
     prohibitive strain energy. For comparison the strain energy estimated for
     the relatively geometrically unrestricted 10 is a sizeable 24.1 kcal/mol.[42]

(50) (a) B. Moisan, A. Robert, and A. Foucand, Tetrahedron, 30, 2867 (1974);
     (b) R. Huisgen, G. Szeimies, L. Mobius, Chem. Ber., 100 2494 (1967); (c)
     W.J. Linn, J. Amer. Chem. Soc., 87, 3665 (1965).

(51) For a comparison with temperatures required for ring opening of unpolarized,
     fused cyclobutenes see ref 47.

(52) In work which is to be reported separately, the enthalpy of reaction $4 \rightarrow 3$
     was found to be 10.4 kcal/mol. This value was determined on a Perkin Elmer
     DSC-2 instrument (isothermal mode, 140°) with samples of 4 in diphenyl ether.
     We are grateful to Mr. R.L. Fyans for making this measurement.

(53) R.C. Dougherty, J. Amer. Chem. Soc., 93, 7187 (1971).

(54) (a) W.G. Dauben, R.L. Cargill, R.M. Coates, and J. Saltiel, J. Amer. Chem. Soc., 87, 3996 (1965); (b) G.S. Hammond, Adv. in Photochem., 7, 373 (1969).

(55) (a) W.G. Dauben, L. Salem, and N.J. Turro, Accounts Chem. Res., 8, 41,(1975); (b) L. Salem, C. Leforesteier, G. Segal, R. Wetmore, J. Amer. Chem. Soc., 97, 479 (1975).

(56) J. Michl, Fortschritte der Chem. Forschung, 46, 1 (1974).

(57) (a) W.Th.A.M. van der Lugt and L.J. Oosterhoff, J. Amer. Chem. Soc., 91, 6042 (1969); (b) The exact nature of the excited state of intended crossing is uncertain without reference to a detailed calculation (including configuration interaction) of the surfaces for $3 \rightleftarrows 4$. The critical point is that there be some singlet state with an appropriate minimum or funnel providing a path for radiationless decay. For a discussion of this specific problem, see ref 56.

(58) The fate of S_1 is probably not this simple. Other species with diradical-zwitterionic character on other thermal surfaces (e.g., canonical forms A and B, geometry unspecified) may be targets for radiationless decay. These species, which connect the open trienes with norcaradiene-like valence isomers and geometric isomers, respectively, are valence isomeric with one another (and species similar to 18). Structures 18a and 18b (and similar representations for A and B) are to be considered resonance contributors to a diradical valence isomer. For a quantitative assessment of radiationless decay as a function of ring size (twisting capability), see H.E. Zimmerman, K.S. Kamm, and D.P. Werthemann, J. Amer. Chem. Soc., 96, 7821 (1974).
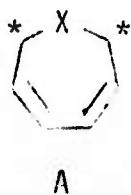
A
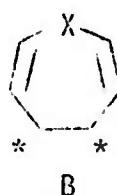
B

(59) Substitution with the dimethylamino group on cycloheptatriene enhances the relative quantum yield of valence isomerization by at least 50,000; A.P. ter Borg and H. Kloosterziel, <u>Chem. Comm.</u>, 1210 (1967).

(60) (a) D.J. Pasto in "Organic Photochemistry," vol. 1, O.L. Chapman, Ed., Marcel Dekker, Inc., N.Y., 1967, p. 155; (b) K. Koch, <u>Adv. Alicyclic Chem.</u>, 1, 258 (1966); Chapman[1b] pointed out at a very early time the importance of a substituent stabilized polar state in the valence photoisomerization of tropones, although it was not clear then whether the intermediate was an excited or ground state species.

(61) Salem[46a] and Michl[56] have pointed out factors for which zwitterions become ground states for diradicals. The two generally available ionic diradical states prefer tight geometry (diminished separation of diradical termini) for the sake of minimized charge separation, while the singlet and triplet non-ionic diradical wave functions are energy minimized at loose geometries in which odd electron density is well separated for diminished electron-electron repulsion.

(62) For a case in which a diradical-zwitterion lies in a calculated 6 kcal/mol well resulting from 90° twist of 1,1-dicyanoethylene, see L. Salem and W.-D. Stohrer, <u>J.C.S. Chem. Comm.</u>, 140, 1975.

(63) For a classic case of trapping by DMAC of a thermally or photochemically generated diradical-zwitterion (an azomethine ylide) with a crude similarity to 18, see ref 6.

(64) C.G. Hatchard and C.A. Parker, <u>Proc. Roy. Soc. (London)</u>, A235, 518 (1956).

Figure. Potential energy surfaces for the photochemical and thermal interconversions of 3 and 4. $\Delta H^{\ddagger}(4 \rightarrow 3, 128°) = 27$ kcal/mol.